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NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

RESEARCH MEMORANDUM

CHEMICAL AND PHYSICAL PROPERTIES OF A BORON-CARBON-HYDROGEN FUEL Z-244 (NACA 55Z8)

By A. E. Spakowski, Patricia M. Cramer, and Marianne Buddie

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SUMMARY

The following chemical and physical properties were determined from a sample of Z-244:

Elemental chemical analysis, percent	
Boron	65.10
Carbon	23.09
Hydrogen	12.38
Net heat of combustion of liquid fuel to gaseous carbon dioxide and water, and solid boric oxide at 25° C, Btu/lb	-25,753
Density, g/ml	
at 0° C	0.8353
at 20° C	0.8242
at 25° C	0.8222
Freezing point	(<-93° C) No true freezing point found
Self-ignition temperature, °C	130
Flash point, °C	45
Vapor-pressure curve	$\log P = -\frac{10,361}{2.303RT} + 7.2754$
Extrapolated boiling point, °C	242
Decomposition, °C	192
Viscosity, centistokes	
-40° C	96.62
0° C	13.73
37.9° C	4.81
Molecular weight	151

Oxygen and water stability were also determined for the fuel.

INTRODUCTION

As part of the Navy Project Zip to consider various boron-containing materials as possible high-energy fuels, the chemical and physical properties of a high-energy fuel Z-244 (NACA 55Z8) prepared by the Olin-

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Mathieson Chemical Company were evaluated at the NACA Lewis laboratory. Elemental chemical analysis, heat of combustion, density, freezing point, self-ignition temperature, flash point, oxygen stability, water stability, vapor pressure and decomposition, viscosity, and molecular weight were determined for the fuel. Although the precision of measurement of these properties was not equal to that obtained for hydrocarbons, this special release research memorandum was prepared to make the data available as soon as possible.

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PROCEDURE AND RESULTS

Chemical analysis. - The fuel, Z-244, was stored and handled in a helium-inerted dry box or under an atmosphere of helium or dry nitrogen to insure against any oxidation prior to the tests. The fuel is a clear, very pale yellow liquid.

The elemental chemical analysis followed the procedures set forth by Project Zip Standard Test Specifications Committee (ref. 1). Total carbon and hydrogen were determined by the microcombustion train to be 23.09 and 12.38 percent, respectively. Total boron was found to be 65.1 percent by the nitric-acid-oxidation method. These values are listed in table I.

Heat of combustion. - A Parr Adiabatic oxygen-bomb calorimeter was used to determine the heat of combustion. The raw heat of combustion was determined by the general method recommended by the Parr Instrument Company with several modifications as described in reference 1. The fuel samples, contained in pyrex glass ampoules, were oxidized in 30 atmospheres of oxygen. The results from five determinations of Z-244 are listed in table II, together with the analysis of the products of combustion and the corrections applied to the raw heating values. The average net heat of combustion of Z-244 was -25,753 Btu per pound based on 25° C reference temperature and liquid fuel going to gaseous carbon dioxide and water, and solid boric oxide.

Density. - The density was determined in an open-arm bicapillary pycnometer with ground-glass caps that were used to effect a seal to the atmosphere. The pycnometer was filled in an atmosphere of nitrogen and then the density measurements were made in the usual manner at three temperatures, 0°, 20°, and 25° C. The densities were 0.8353, 0.8242, and 0.8222 gram per milliliter, at 0°, 20°, and 25° C, respectively.

Freezing point. - The freezing-point behavior was studied in an apparatus with a motor-driven reciprocating stirrer and a Beckman mercury thermometer. No true freezing point was obtained. However, upon cooling the sample of Z-244 to -93° C, the stirrer was stopped by the increased viscosity of the fuel. Upon further cooling with liquid nitrogen a brittle glass-like material was produced. No significant temperature measurements were made in this lower range.

Self-ignition temperature. - The self-ignition temperature was determined in the Setchkin apparatus (ref. 2). Ignition attempts were made as the temperature was decreased with the same flask being used without cleaning between ignitions. When the lowest point giving ignition was reached, the value was rechecked using a series of clean flasks. The self-ignition temperature obtained was 130° C.

Flash point. - The flash point was determined in the NACA modified Pensky-Martens type closed-cup apparatus. The sample cup has a volume of 3 cubic centimeters and is half filled with the liquid sample. The temperature rise of the cup was held to less than 1° C per minute. The flash point obtained was 45° C.

Oxygen stability. - The oxygen stability of Z-244 was determined in an apparatus similar to one described in reference 3. The apparatus was, however, placed in a constant-temperature air bath held at 29.5° C. Five milliliters of Z-244 were placed in the 50-milliliter modified Erlenmeyer flask previously flushed with dry nitrogen. The connecting stopcock was then opened to 75 milliliters of oxygen in a gas burette. This stability test is based on the assumption that the rate of reaction between the fuel and oxygen is proportional to the rate at which oxygen is used up as measured by the volume change in the burette. It is also assumed that only liquid and solid products are formed.

In figure 1 the volume decrease of the gaseous system is plotted against the time after opening the stopcock permitting the oxygen to diffuse into the fuel flask. A continual decrease in total volume is noted for the first 225 hours, after which the rate of decrease levels off. The test is rather difficult to interpret because varying amounts of hydrogen and ethane are evolved while the oxygen is being consumed. Thus the consumption rate of oxygen is actually higher than presented.

Water stability. - The water stability of Z-244 was determined with an excess of water and with vigorous stirring to ensure a large contact area between the fuel and water. Five grams of the fuel were placed in the apparatus previously flushed with dry nitrogen and 100 grams of water added with vigorous stirring. There was an immediate reaction which slowed down after several minutes. In figure 2 the water stability data are presented graphically. The volume of hydrogen liberated per gram of fuel is plotted against the time in hours. After the initial rapid release of hydrogen, the reaction slowed down for 10 hours. Then the reaction rate increased to 0.79 milliliter hydrogen per gram of fuel per hour and remained constant until the end of the first week (168 hrs). From this point the rate began to decrease very slowly.

Vapor pressure and decomposition. - The vapor pressure and thermal stability of the high-energy fuel were determined in an isoteniscope shown in figure 3. The isoteniscope was flushed with helium and one milliliter of Z-244 admitted into the sample bulb with a long-needled syringe. Points A and B were then sealed in order while the sample was frozen at -196° C and the apparatus evacuated. The isoteniscope was then connected to a mercury manometer system and placed in a clear silicone oil bath. The circulating oil bath was heated at a rate less than 1° C per minute. The pressure and temperature measurements were recorded at 10-15 minute intervals. 4050

The results are shown in figure 4, where the pressure in millimeters is plotted against the temperature in °C. The first part of the curve is a measure of the vapor pressure of the fuel. As the temperature increases, if the fuel sample begins to decompose, the pressure of the gaseous decomposition products is added to the pressure of the fuel. The dashed line in figure 4 is the expected true vapor pressure of Z-244 at the elevated temperatures.

In order to determine the temperature at which Z-244 begins to decompose, the log of the pressure in millimeters is plotted against the reciprocal of the temperature in °K in figure 5. The straight-line portion of the curve represents the measurement of the vapor pressure of the fuel alone. At about 192° C the fuel begins to decompose and adds to the total pressure.

The equation for the straight-line portion of the vapor-pressure curve between 70° and 190° C in figure 5 is

$$\log P = -\frac{10{,}361}{2.303RT} + 7.2754$$

where

P pressure, millimeters of mercury

T temperature, °K

R gas constant

The mean molar heat of vaporization over the temperature range covered by the straight-line portion of the curve is 10,361 calories. By extrapolating to a pressure of 760 millimeters of mercury, a boiling point of 242° C was obtained.

Viscosity. - The viscosity of Z-244 was measured over a range of temperatures with a series of Cannon-Manning semi-micro viscometers. The viscosities were determined in the usual manner with one modification.

Dried nitrogen was used as an inert blanket during the runs to eliminate any oxidation of the sample. As a further check duplicate runs were made with the same sample at each temperature. The viscosities measured at -40°, 0°, and 37.8° C were 96.62, 13.73, and 4.81 centistokes, respectively. Viscosity measurements were attempted at 60° C (140° F), but were unsuccessful. At this temperature the viscosity of the fuel increased with time due to changes in the fuel sample. The viscosity-temperature details are plotted in figure 6.

Molecular weight. - The molecular weight of the fuel was estimated by a freezing-point depression technique with cryoscopic benzene as the solvent. The average molecular weight of a pair of determinations was 151. The accuracy of the method is within 2 percent.

DISCUSSION

Any material being considered as a high-energy fuel must of necessity have a readily available high heat content. The heat of combustion of Z-244 as determined by the oxygen-bomb calorimeter was -25,753 Btu per pound. The heat of combustion, calculated from the boron-carbon-hydrogen analysis and assuming values for the bond energies involved, is -26,090 Btu per pound. Thus Z-244 would be quite suitable for engine development work due to its high heat of combustion. The high boron content would also permit the investigation of problems associated with the deposition of boron oxides on the engine components.

The boiling point and vapor pressure of the fuel are similar to that of a C_{13} hydrocarbon and are thus in the range considered for aircraft fuels. The marked increase in viscosity of Z-244 at -93° C (-135° F) would possibly create a problem in fuel systems under certain low-temperature operations. However, this would not seriously affect the engine development studies.

Although the self-ignition temperature of Z-244 (130° C) is much lower than that of hydrocarbons with similar boiling points (decane and hexadecane have self-ignition temperatures of about 230° C), the material can be handled in air under normal conditions. From other tests it appears that both time and temperature play an important role in the stability of this fuel. During the stability test when the temperature was raised 1° C per minute, the fuel began to decompose at a temperature of 192° C. On a similar material when the temperature-rise rate was lowered to about 0.5° C per minute, decomposition set in at 160° C. In the viscosity determination where the fuel is held for a relatively long period of time at one temperature, it was found that some decomposition (or perhaps oxidation) occurred at temperatures as low as 60° C. It was shown in the oxygen stability test that after the fuel was exposed approximately 225 hours to an atmosphere of oxygen, the consumption of oxygen decreased to zero. Actually the fuel had developed a gelatinous surface film, and this film probably halted any further reaction.

The flash point of 45° C for Z-244 is considerably lower than for hydrocarbons of similar volatility. Dodecane and tetradecane have flash points of 74° and 100° C, respectively.

On the basis of the relatively few tests performed, it appears that a fuel having the physical and chemical properties of Z-244 may be suitable for engine development. Considerably more information must be obtained, however, before the fuel's capabilities in propulsion applications can be determined. 4050

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, February 2, 1956

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1. Callery Chemical Company, ed.: Project Zip Standard Specifications Committee: Standard Test Specifications for BCF Materials. Second edition.

2. Setchkin, Nicholas P.: Self-Ignition Temperatures of Combustible Liquids. Jour. Res. Nat. Bur. Standards, vol. 53, no. 1, July 1954, pp. 49-66.

3. Korzun, A. G.: Certain Physical and Chemical Properties of Ethylene-Decaborane Reaction Products. MCC-1023-TR-70, Mathieson Chem. Co., Aug. 1954.

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TABLE I. - CHEMICAL AND PHYSICAL PROPERTIES OF Z-244 (NACA 5528)

Elemental analysis:	
Boron, percent	65.10
Carbon, percent	23.09
Hydrogen, percent	12.38
Heat of combustion, Btu/lb	-25,753 (at 25° C)
Density, g/ml	0.8353 at 0° C 0.8242 at 20° C 0.8222 at 25° C
Freezing point	No true freezing point found
Self-ignition temperature, °C	130
Flash point, °C	45
Vapor pressure	$\log P = -\frac{10,361}{2.303RT} + 7.2754$
Boiling point (extrapolated), °C	242
Decomposition, °C	192
Viscosity, centistokes	96.62 at -40° C 13.73 at 0° C 4.81 at 37.9° C
Molecular weight	151

TABLE II. - HEAT OF COMBUSTION OF Z-244*

Determination	1	2	3	4	5
Sample weight, g	0.4613	0.5070	0.4067	0.4380	0.4787
Percent boron burned	56.5	52.2	57.8	57.6	53.0
Percent carbon burned	74.8	74.8	83.5	75.8	71.5
Raw heat, Btu/lb	-19,538	-18,597	-19,620	-19,744	-18,972
Corrections, cal/g:					
To atmospheric pressure for oxygen consumed	-2.5	-2.4	-2.6	-2.6	-2.5
Constant volume to constant pressure	-33.3	-32.2	-33.6	-33.6	-32.3
Hydration solution of boron oxide	299.6	276.5	305.7	305.6	280.6
Vaporization of water	651.2	651.2	651.2	651.2	651.2
Unburned boron	-3983.0	-4345.2	-3847.3	-3847.3	-4224.5
Unburned carbon	-467.5	-467.5	-311.6	-457.7	-535.7
Total corrections, cal/g	-3535.5	-3919.6	-3238.2	-3384.4	-3863.2
Btu/lb	-6363.7	-7055.3	-5828.8	-6092.0	-6953.8
Net heat of combustion, Btu/lb	-25,902	-25,652	-25,449	-25,836	-25,926
Average ΔH_C		-25,753			

*Elemental analysis: Percent boron, 65.1; percent carbon, 23.09; percent hydrogen, 12.38.

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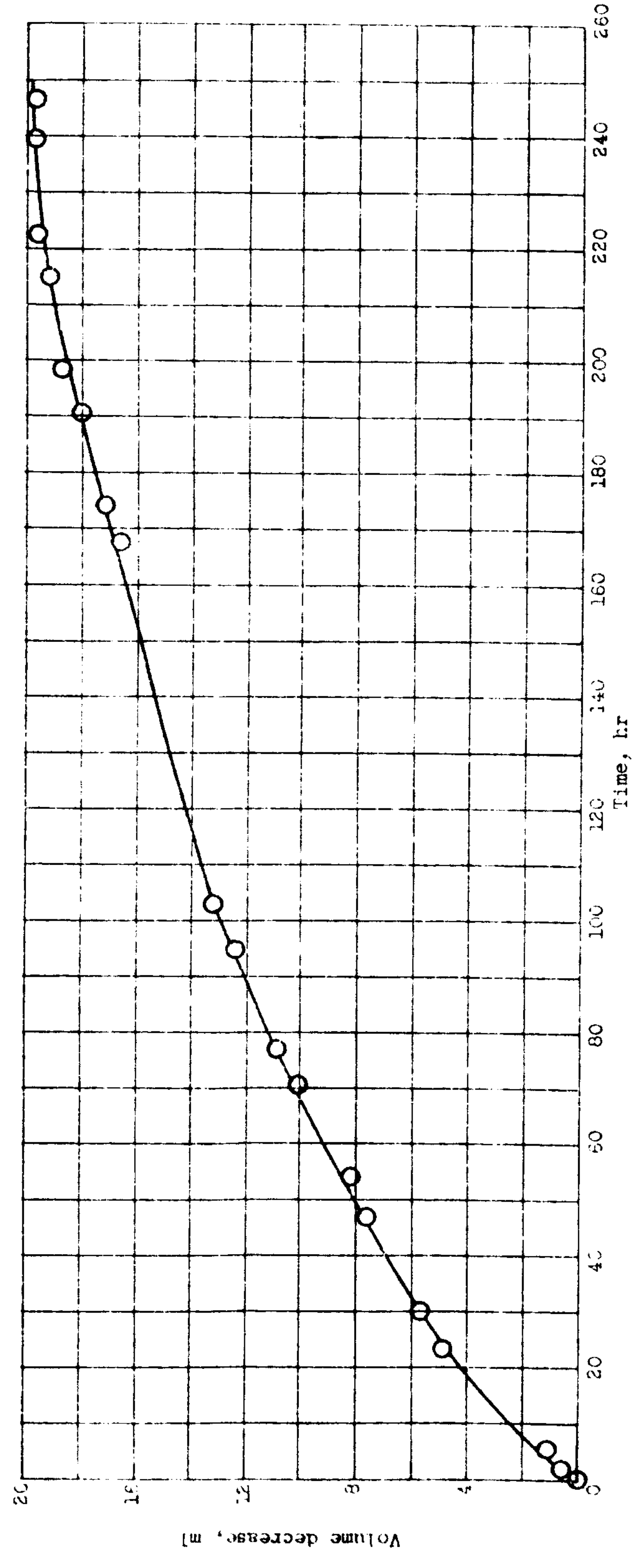

Figure 1. - Oxygen stability of Z-244 at 29.5° C.

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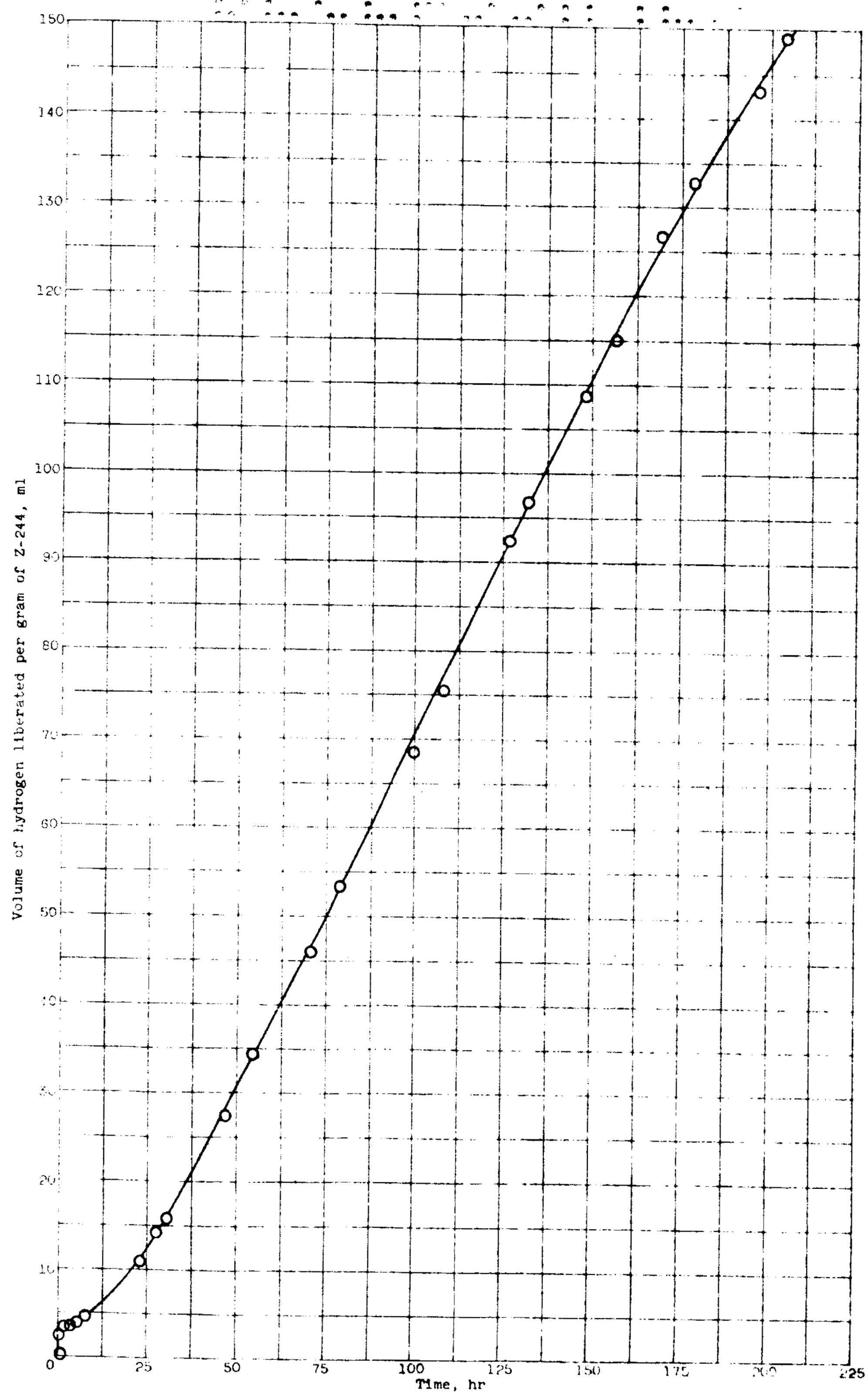

Figure 2. - Water stability of Z-244 at 27° C.

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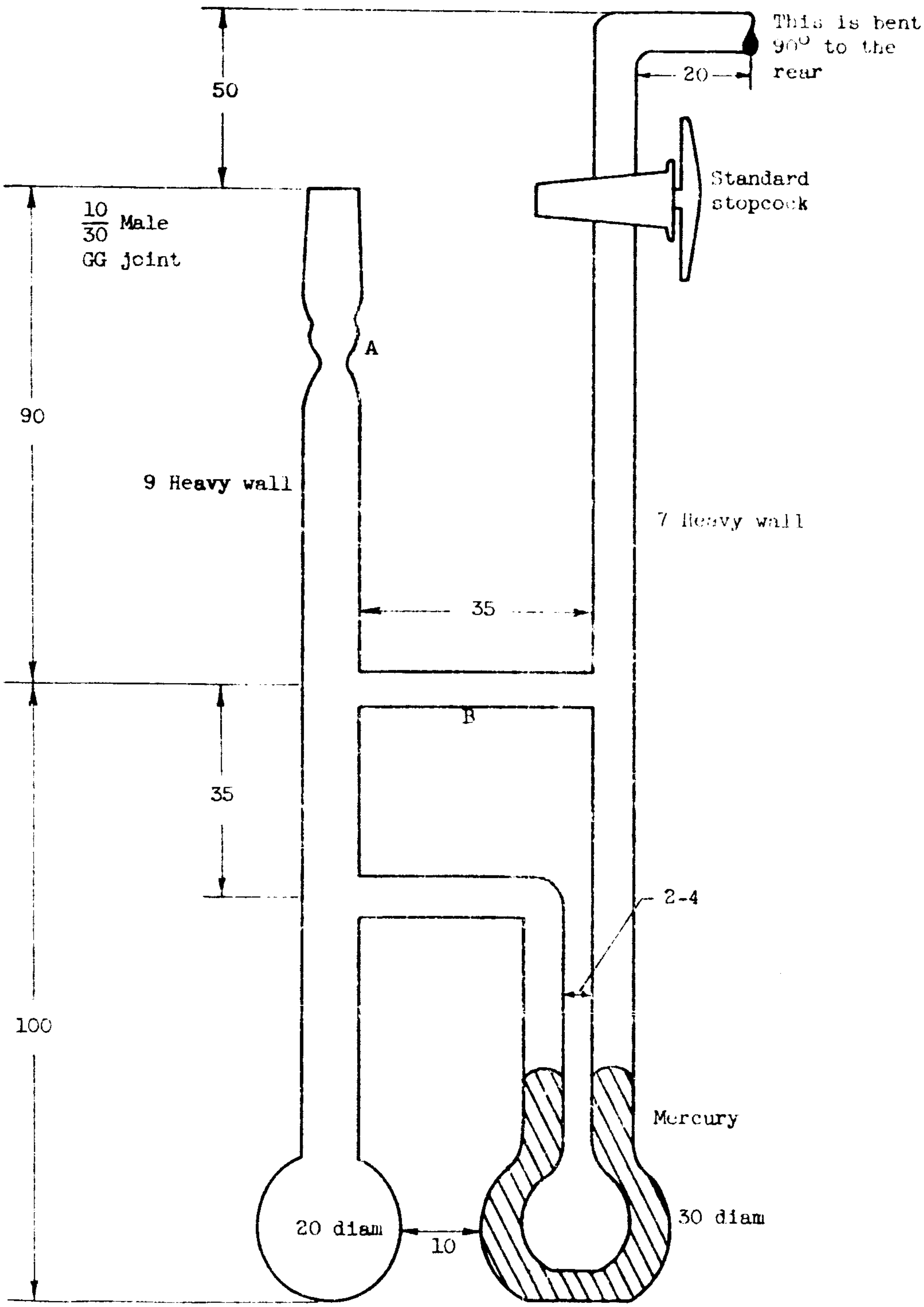

Figure 3. - NACA isoteniscope for vapor pressure studies. (All dimensions in mm.)

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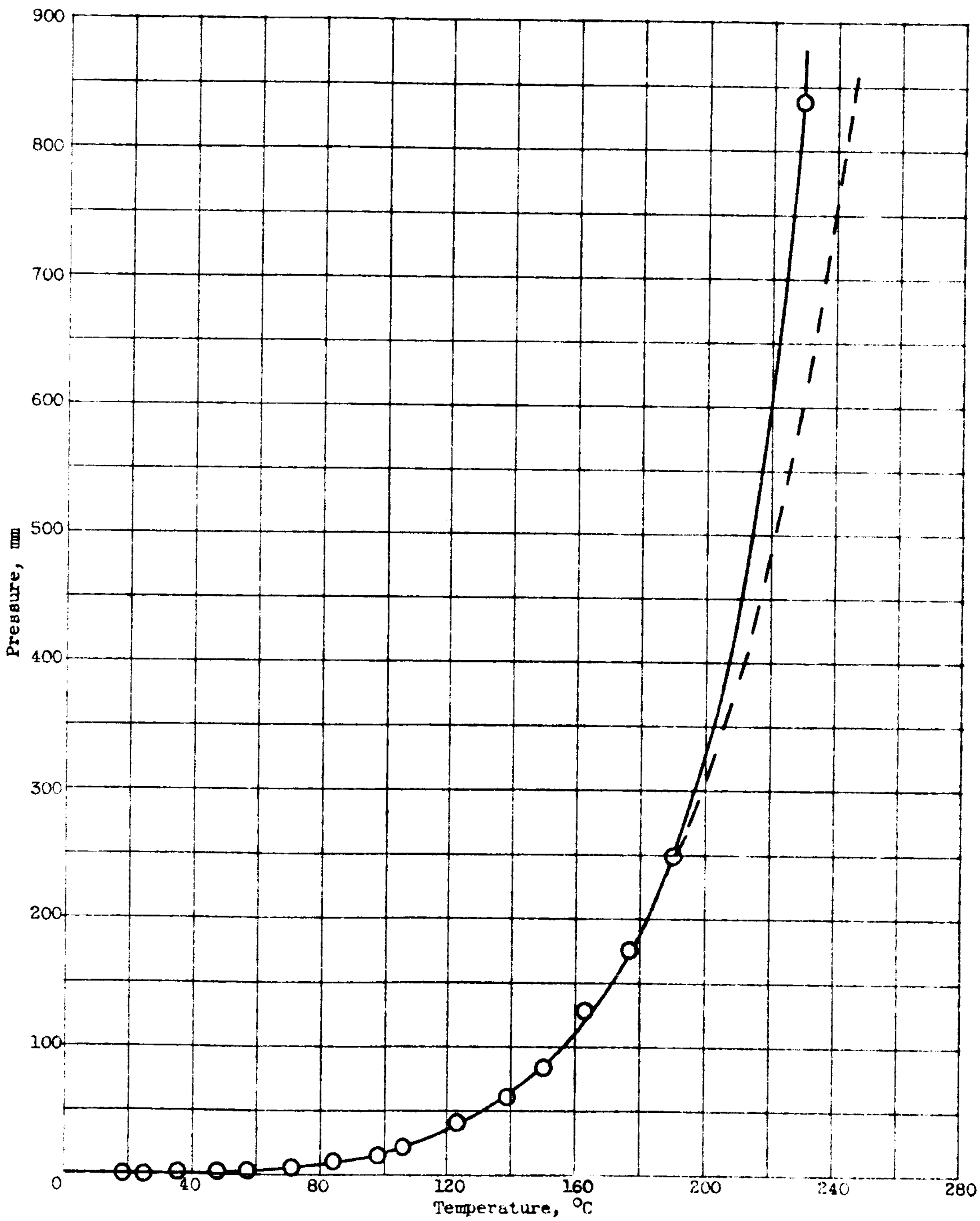

Figure 4. - Vapor pressure developed by Z-244 with increasing temperature.

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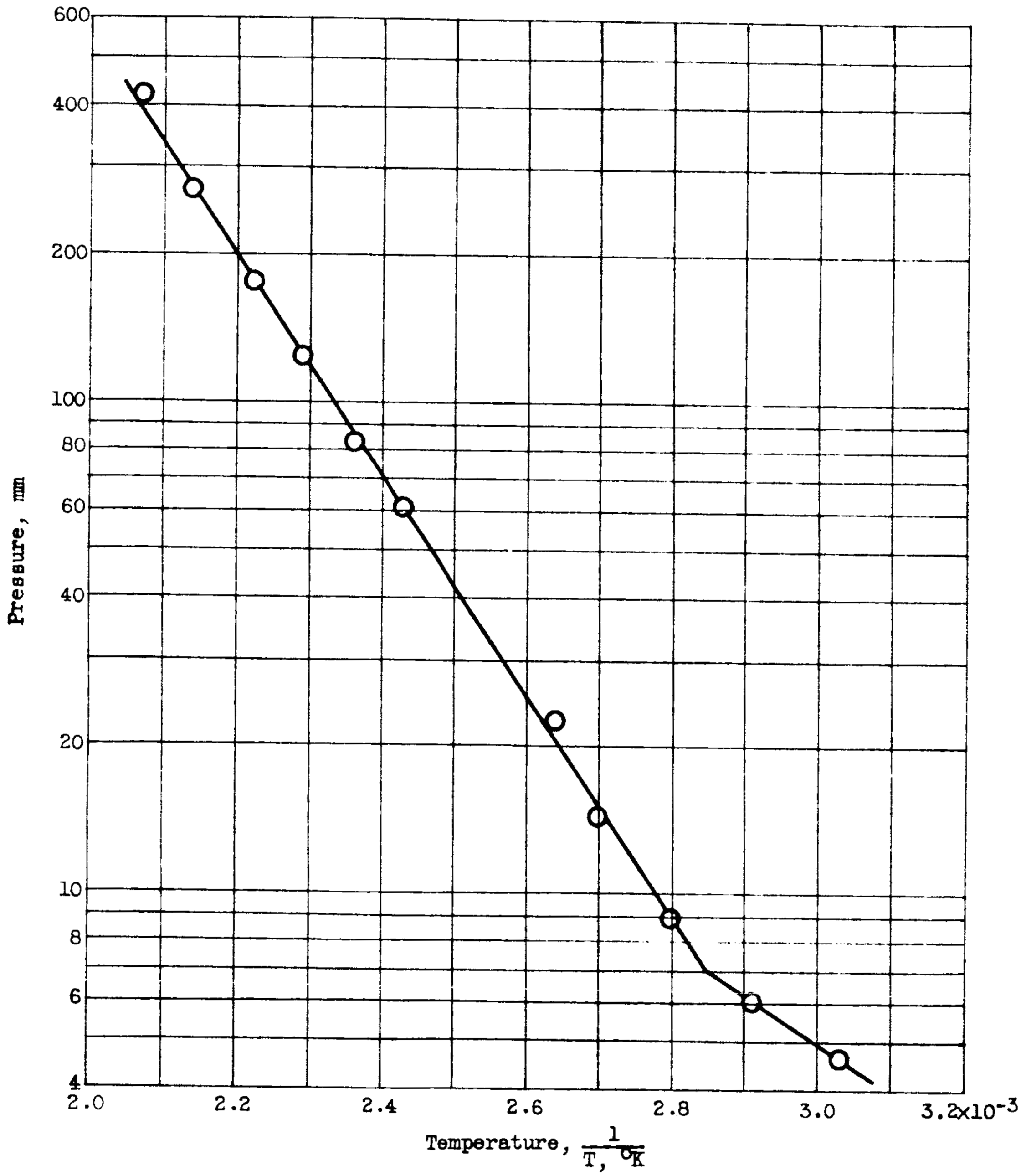

Figure 5. - Pressure-temperature relation for Z-244.

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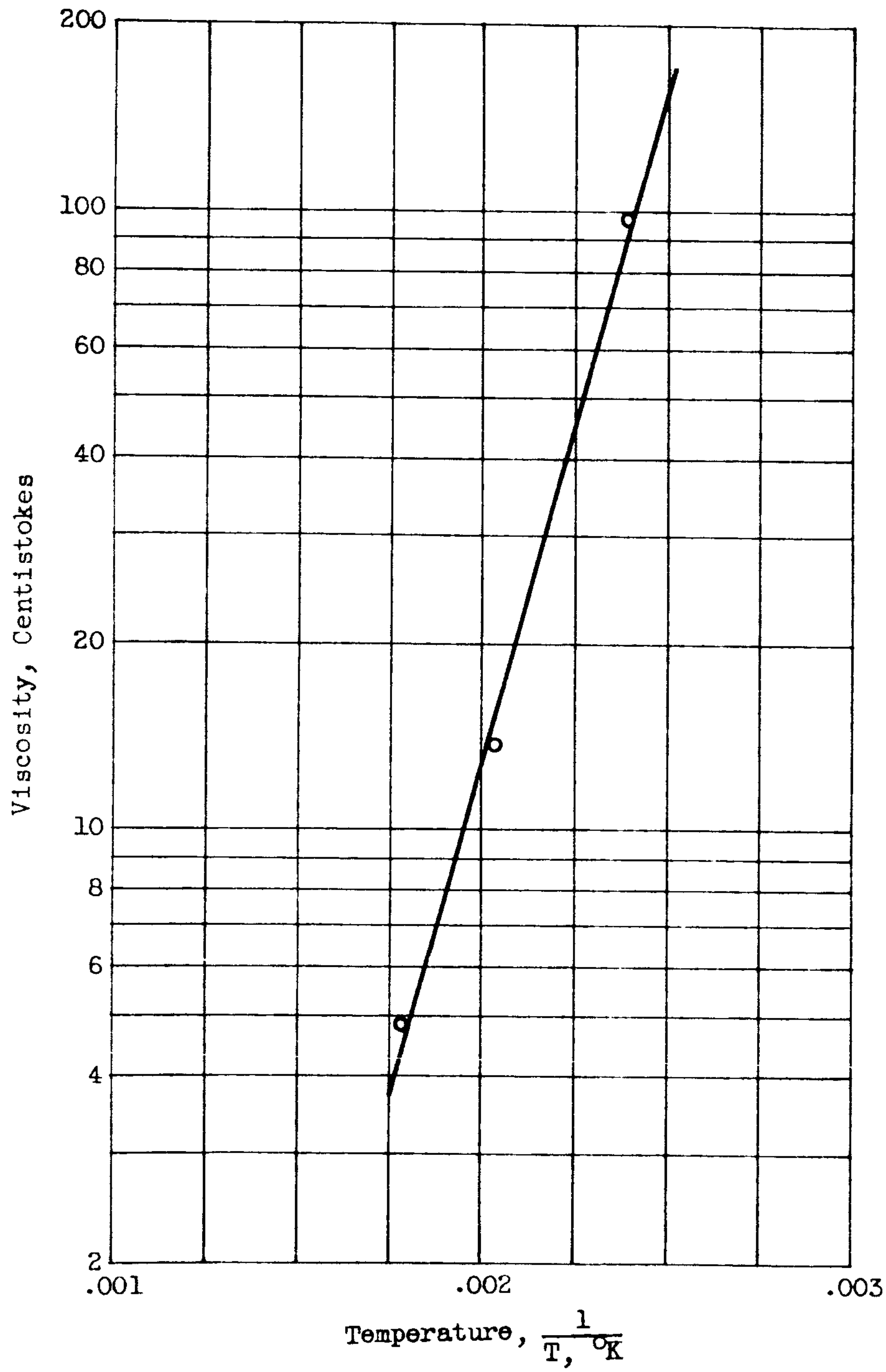

Figure 6. - Viscosity-temperature relation of Z-244.

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CHEMICAL AND PHYSICAL PROPERTIES OF A BORON-CARBON-HYDROGEN

FUEL Z-244 (NACA 55Z8)

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Fuels - Properties, Physical and Chemical 3.4.2

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CHEMICAL AND PHYSICAL PROPERTIES OF A BORON-CARBON-HYDROGEN FUEL Z-244 (NACA 55Z8)

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Abstract

A boron-carbon-hydrogen fuel, Z-244, (prepared by Olin-Mathieson Chemical Company) was evaluated on the following properties: elemental analysis, heat of combustion, density, freezing point, self-ignition temperature, flash point, vapor pressure and decomposition, viscosity, oxygen and water stability, and molecular weight.

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